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Effect of microwave annealing temperatures on lead zirconate titanate thin films

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Abstract
Lead zirconate titanate ($Pb_{1.1}(Zr_{0.52}Ti_{0.48})O_3$) thin films of thickness 260 nm on Pt/Ti/SiO_2/Si substrates were densified by 2.45 GHz microwave annealing. The PZT thin films were annealed at various annealing temperatures from 400 to 700 °C for 30 min. X-ray diffraction showed that the pyrochlore phase was transformed to the perovskite phase at 450 °C and the film was fully crystallized. The secondary (again pyrochlore) phase was observed in the PZT thin films, which were annealed above 550 °C. The surface morphologies were changed above 550 °C of the PZT thin films due to the secondary phase. Higher dielectric constant (ε_r) and lower dielectric loss coercive field (E_c) were achieved for the 450 °C film than for the other annealed films.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, piezoelectric thin films have attracted considerable attention since they are one of the essential materials in microfabricated devices such as microsensors and microactuators. In particular, $Pb(Zr_xTi_{1-x})O_3$ (PZT) with a composition near the morphotropic phase boundary (MPB) is a well-known material for its excellent ferroelectricity and piezoelectricity. The ferroelectric perovskite phase generally forms in $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films at over 600 °C [1]. These high temperatures seriously damage the stack, leading to interdiffusion between the elements of the film and the substrate [2], and the evaporation of lead oxide from the surface of film causes loss of the film's stoichiometry. Therefore, decreasing the processing temperature for the ferroelectric thin films has been the goal for researchers. Many groups have been attempting to prepare PZT thin films at low temperature by various techniques such as electrophoretic deposition [3], hydrothermal synthesis [4], rf sputtering [5], sol–gel process [6], CO_2 laser annealing [7], metal–organic chemical vapor deposition [8] and millimeter wave annealing [9].

The use of microwave energy for processing materials has recently become an attractive area for research and innovation [10, 11]. The growing interest during the past decade is essentially due to the possibility of reduction in manufacturing cost through energy savings, shorter processing times and improved product uniformity and yields. Microwave processing differs mainly in that the heat is generated within the material, instead of in an external heating source, which fact is responsible for the unique microstructure and uniformity. Microwave processing has been used in annealing ferroelectric/dielectric thin films. Ahn and his colleagues [12] studied the crystallization of an amorphous silicon (a-Si) film

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in a very short time (2 h) by the microwave process (2.45 GHz), in contrast to more than 40 h required by the conventional process at the same temperature. Zanetti *et al* [13] reported that the time required to crystallize $SrBi_2Ta_2O_9$ (SBT) thin films thoroughly was drastically reduced (700 °C/10 min) when a domestic microwave oven was used, rather than a conventional furnace (700 °C/2 h). Vasconcelos *et al* [14] reported that a domestic microwave oven (2.45 GHz) enhanced the crystallization of $SrBi_2Nb_2O_9$ (SBN) thin film at 700 °C for 30 min than the conventional annealed SBN thin film at 700 °C for 2 h. Song and his coworkers [15] completely formed a perovskite phase PZT thin film using the multi-mode cavity of 2.45 GHz microwaves at a lower temperature (600 °C) than required to form a conventionally annealed PZT thin film (700 °C). Its dielectric loss was lower and the remnant polarization was higher than that of a conventionally annealed PZT thin film. However, neither lower processing temperature (<500 °C) nor the effect of annealing temperatures on PZT thin films using 2.45 GHz microwaves has been reported.

The comparison of microwave and conventional annealing of PZT films has been reported earlier by us [16]. This study reports the effect of microwave annealing temperatures on the PZT thin films which were deposited on a $Pt/Ti/SiO_2/Si$ substrate using the single-mode cavity of 2.45 GHz microwaves. The PZT thin films were annealed at various temperatures from 400 to 700 °C for 30 min. The crystal structure, the surface morphology and the electrical properties of PZT thin films were investigated. Based on the experimental results, the effects of microwave annealing temperatures on the PZT thin films were discussed.

2. Experimental procedures

2.1. Preparation of PZT thin films

PZT thin films were prepared by the sol–gel method. The lead acetate trihydrate ($C_4H_6O_4Pb{\cdot}3H_2O$) was dissolved in 2-methoxyethanol ($CH_3OCH_2CH_2OH$); the solutions were heated to 110 °C, and then refluxed for 2 h. The solutions were cooled to 90 °C before the required quantities of zirconium-*n*-propoxide ($Zr(C_3H_7O)_4$) and 2-methoxyethonal were added sequentially and refluxed for 1 h. Titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) was added to the same as zirconium-*n*-propoxide processing for 2 h. Clear light yellow PZT stock was formed by air-cooling to room temperature. The solution was stable and no precipitation formed for several months. The concentration of the final solution could be adjusted to 0.2 M by adding or distilling an appropriate quantity of solvent. The precursor solution was entirely prepared in an ambient atmosphere. The nominal composition of the solution was Pb:Zr:Ti = 1.1:0.53:0.47. $Pt/Ti/SiO_2/Si$ substrates, which provide the nucleation sites for the perovskite phase because of good lattice matching, were selected [17]. The precursor solution was deposited on the $Pt/Ti/SiO_2/Si$ substrates by spin-coating at 500 rpm for 1 s, and 3000 rpm for 15 s. The as-deposited layer was dried on a hot plate in air at 150 °C for 5 min and decomposed at 400 °C for 10 min to evaporate the alcohol and organics. The decomposition temperature was established by the thermogravimetric analysis (TGA) results, which indicates that at 400 °C most of the organics evaporated and decomposed from the PZT thin films. The spin coating and drying process were repeated six times to obtain the desired thickness of 260 nm.

2.2. Processing of PZT thin films

The PZT thin film was placed in the casket, which was thermally insulated. The casket was located at the center of the highest electric field in the applicator. SiC rods were used as susceptors because PZT does not absorb 2.45 GHz microwaves at room temperature [18]. The microwave energy initially heated the SiC rods, which, in turn, transferred heat to the insulation and eventually to the thin film [19]. As the temperature of the PZT thin film increased, it more effectively coupled with the microwave energy, thus promoting direct heating. The microwave frequency was 2.45 GHz and the power was adjusted from 400 to 700 ± 50 W to maintain the annealing temperature from 400 to 700 °C. The temperature was controlled to within ±1 °C by continuously adjusting the power of the microwave. The temperature was measured using a thermocouple (Pt & 87%Pt–13%Rh) with an alumina sheath, which was in contact with the surface of the film.

2.3. Characterization of PZT thin films

The crystallization and the phase formation of all the annealed films were examined at room temperature with an x-ray diffraction (XRD) system (Rigaku D/MAX-IIB at 40 kV and 30 mA), Cu Kα radiation wavelength $\lambda = 1.5405$ Å in the glazing angle (1°), every 0.02° between $2\theta = 20°$ and 60°. The film thickness, surface morphologies and cross sections of the PZT thin films were examined using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F). The surface roughness of PZT thin films was characterized using an atomic force microscope (AFM) system (Seiko Instruments Inc. SPI3800N). Au electrodes were deposited by rf sputtering on the top surface of PZT thin films through a shadow mask with a diameter of 1 mm for electrical measurements. This deposition was conducted at room temperature. The dielectric properties were measured at 1 kHz using an impedance analyzer (HP impedance/gain analyzer 4194 A). The polarization–electric (P–E) hysteresis loops were measured using a Radiant Technologies RT-66A ferroelectric test system by applying triangular voltages at a frequency of 2 kHz.

3. Results

3.1. Crystalline phase of PZT thin film

Figure 1(a) shows the XRD patterns of PZT thin films annealed using 2.45 GHz microwaves at various temperatures from 400 to 700 °C for 30 min. The PZT thin film crystallized at 400 °C exhibits the perovskite phase, but still has the pyrochlore phase; it seemed that the temperature of the PZT thin film was not enough for the formation of a complete perovskite phase. The pyrochlore phase exists as an intermediate phase between the amorphous and the perovskite phase of the PZT thin films [1, 20]. As the annealing temperature was increased to 450 °C the pyrochlore phase disappeared and was transformed to the perovskite phase. The PZT thin films crystallized at

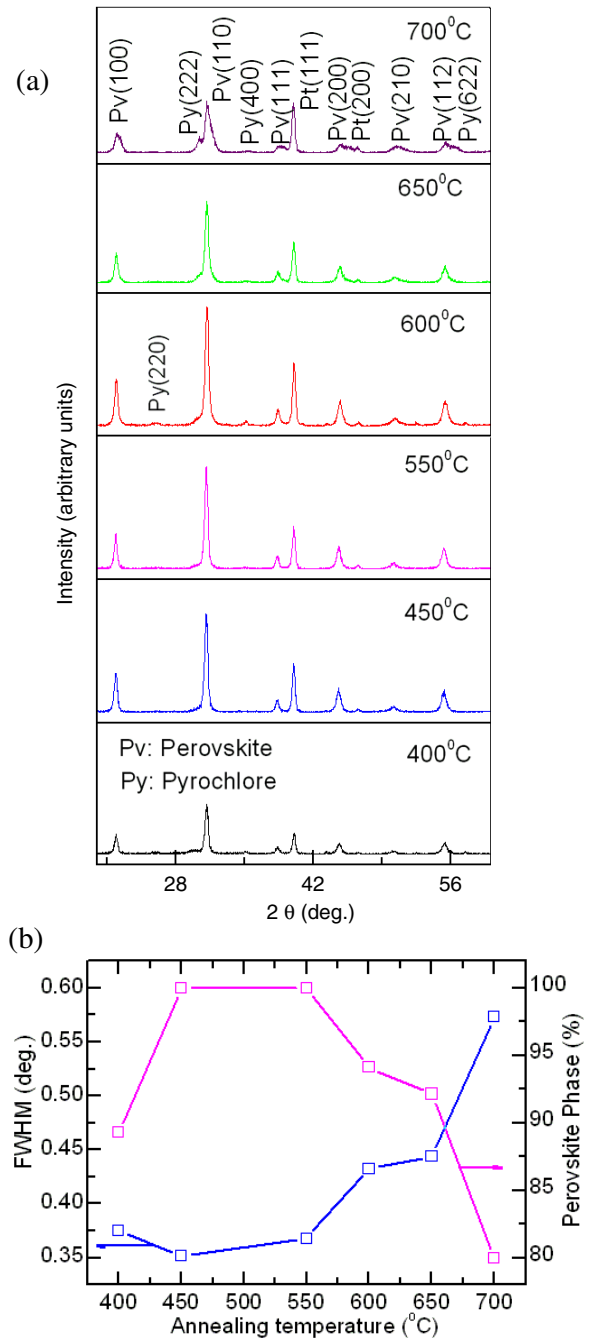

Figure 1. (a) XRD patterns of PZT thin films as a function of annealing temperature, (b) percentage of perovskite phase and FWHM of (110) peaks as a function of the annealing temperature.

450 °C and 550 °C show a complete perovskite phase without any pyrochlore phase. The PZT thin film crystallized at 600 °C shows trace amounts of pyrochlore phases (Py(220), Py(400) and Py(622)) due to PbO volatilization [21]. When the annealing temperature was increased further to 700 °C, the pyrochlore phases were enhanced. The peaks with the highest intensity in the x-ray diffraction patterns of PZT thin films were indexed as the (110) plane, indicating that the films were mostly randomly oriented, which agreed with earlier reports [9, 15]. Kwok and Desu [22] reported that whenever the second phase such as pyrochlore was formed, the pyrochlore to perovskite conversion occurs through an interface-controlled transformation by isotropic growth, and that the resultant films had a random orientation with a strong (110) PZT reflection. These results suggest that the microwave annealing conditions strongly influence the crystallization behavior of PZT thin films.

The formula of $100 \times I_{pv}/[I_{py} + I_{pv}]$ is used to calculate the percentage of the perovskite phase, where I_{pv} is the XRD intensities of the perovskite phase peaks and I_{py} is the XRD intensities of the pyrochlore phase peaks, respectively. Figure 1(b) shows the percentage of the perovskite phase as a function of the annealing temperature. The percentage of the perovskite phase rises initially up to 450 °C due to the phase transformation between the pyrochlore and the perovskite phase, beyond which it saturates up to 550 °C due to the complete perovskite phase, and then it decreases due to the formation of the secondary phase in the films, as indicated in the XRD pattern (figure 1(a)). All of the characteristic peaks of PZT, especially the (110) peak, become much stronger and sharper as the annealing temperature increases. The full width at half-maximum (FWHM) is considered in evaluating the quality of the PZT thin film [23, 24]. Figure 1(b) indicates the FWHM of the perovskite phase peak (110) as a function of the annealing temperature. The PZT thin films crystallized at a lower temperature have a narrower FWHM than those crystallized at a higher temperature [25]. These results indicate that the lower annealing temperature of PZT thin films shows better crystallinity and higher quality of films than the higher annealing temperature of PZT thin films. However, the higher annealing temperature leads to PbO volatilization, which reduces the quality of PZT thin films.

3.2. Surface morphology of PZT thin films

We examined the surface morphologies of PZT thin films by the field-emission scanning electron microscope (FE-SEM). Figure 2 shows the surface morphologies of PZT thin films, which were crystallized at (a) 400 °C, (b) 450 °C, (c) 550 °C, (d) 600 °C and (e) 700 °C using 2.45 GHz microwaves. The PZT thin film crystallized at (a) 400 °C shows much smaller grains than the other annealed PZT thin films due to the pyrochlore phase, as indicated in the XRD pattern (figure 1(a)). The PZT thin films crystallized at (b) 450 °C and (c) 550 °C show denser and finer grains and the grains were uniform. The PZT thin film crystallized at (d) 600 °C shows large grains and small grains with pores. The image of the region of the small grains was enlarged, clearly revealing dense grains. The large grain sizes were increased with pores at 700 °C (e) of PZT thin films. The large grains were associated with the secondary phase [26] and the composition of the PZT thin film might be changed [21]. The XRD pattern (figure 1(a)) and the percentage of perovskite phase (figure 1(b)) indicate the presence of a secondary phase in these films. Figure 2(f) reveals the cross-sectional FE-SEM image of the 450 °C PZT thin film with multilayered PZT, Pt, Ti, SiO_2 and Si structures as well as the interface between the PZT film and the bottom electrode (Pt). The image reveals the very clear interfaces between the layers. The thickness of the PZT thin films was about 260 nm.

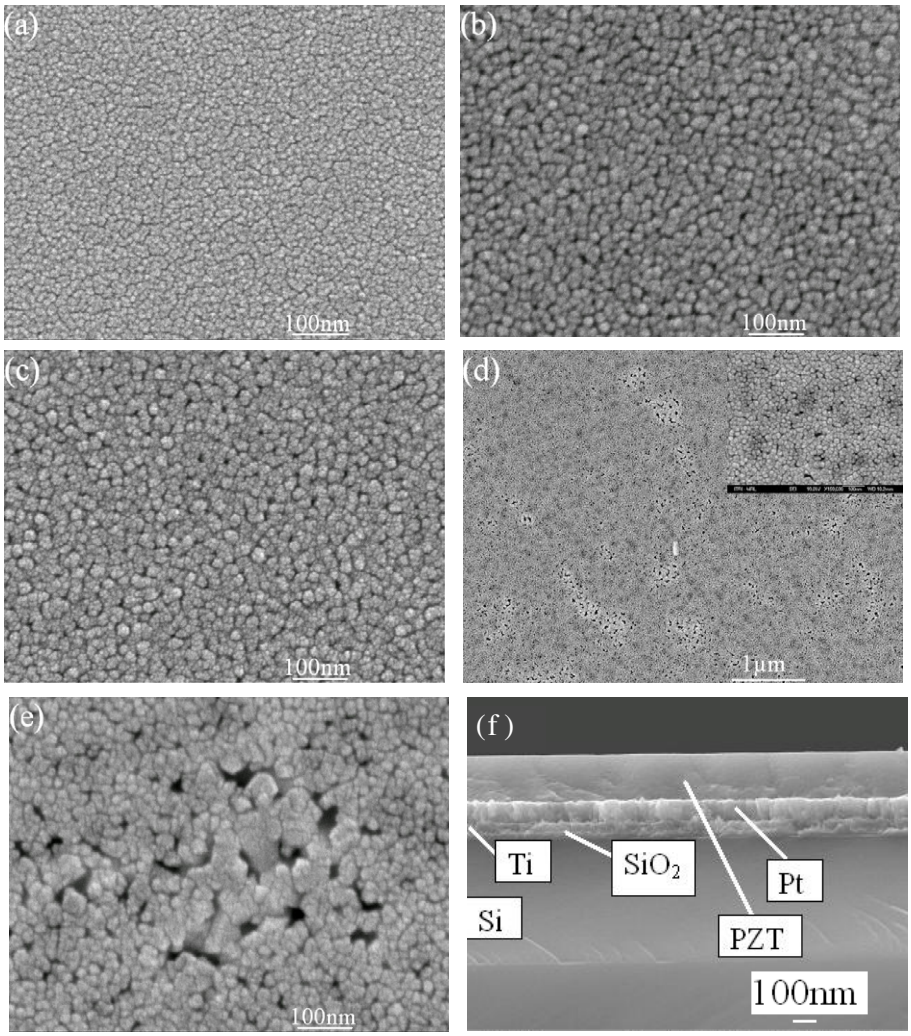

Figure 2. FE-SEM images of PZT thin films were crystallized at (a) 400 °C, (b) 450 °C, (c) 550 °C, (d) 600 °C, (e) 700 °C and (f) cross section at 450 °C film.

The surface roughness and the three-dimensional image of PZT thin films were also examined by atomic force microscopy (AFM). Figure 3 shows the typical three-dimensional images of PZT thin films crystallized at (a) 400 °C, (b) 450 °C and (c) 600 °C using the microwave process. The PZT thin film crystallized at (b) 450 °C shows larger grains and more uniformly distributed than those in other microwave-annealed films. The PZT thin film crystallized at (c) 600 °C shows non-uniform morphology due to the PbO volatilization [27], which is also indicated in figure 2. Furthermore, for the R_a and R_{rms} measured by AFM, R_a is the average roughness and R_{rms} is the root mean square roughness. Figure 4 shows the roughness parameters (R_a, R_{rms}) and average grain size as a function of the annealing temperature. The surface roughness was increased between 400 and 450 °C and was less than 0.5 nm (R_{rms}) and 0.4 nm (R_a), and is associated with the phase transformation from the pyrochlore phase to the perovskite phase, as indicated in the XRD pattern (figure 1(a)) and the FE-SEM images (figure 2). The surface roughness was almost constant between 450 and 550 °C because of the complete formation of the perovskite phase. From 550 to 700 °C, values of 2.98 nm (R_{rms}) and 2.25 nm (R_a) have been due to the volatilization of PbO [21]. These results suggest that the surface roughness is closely related to the annealing temperature of PZT thin films.

3.3. Electrical properties of PZT thin films

Figure 5 exhibits the dielectric properties of the PZT thin films measured at 1 kHz as a function of the annealing temperature. The dielectric constant decreases and the dissipation factor increases beyond the temperature of 550 °C were believed to be due to the volatilization of PbO. Figure 6 shows the polarization electric (P–E) hysteresis loops as a function of the annealing temperature. Shapes of the hysteresis loops were reasonably square and exhibit excellent saturation up to 550 °C, after which these shapes changed, reflecting the difference in crystallinity, as shown in the XRD pattern (figure 1). Figure 7 shows the trend of the remnant polarization (P_r) and coercive field (E_c) as a function of the annealing temperature. The E_c initially decreased with temperature between 400 and 450 °C, beyond which it

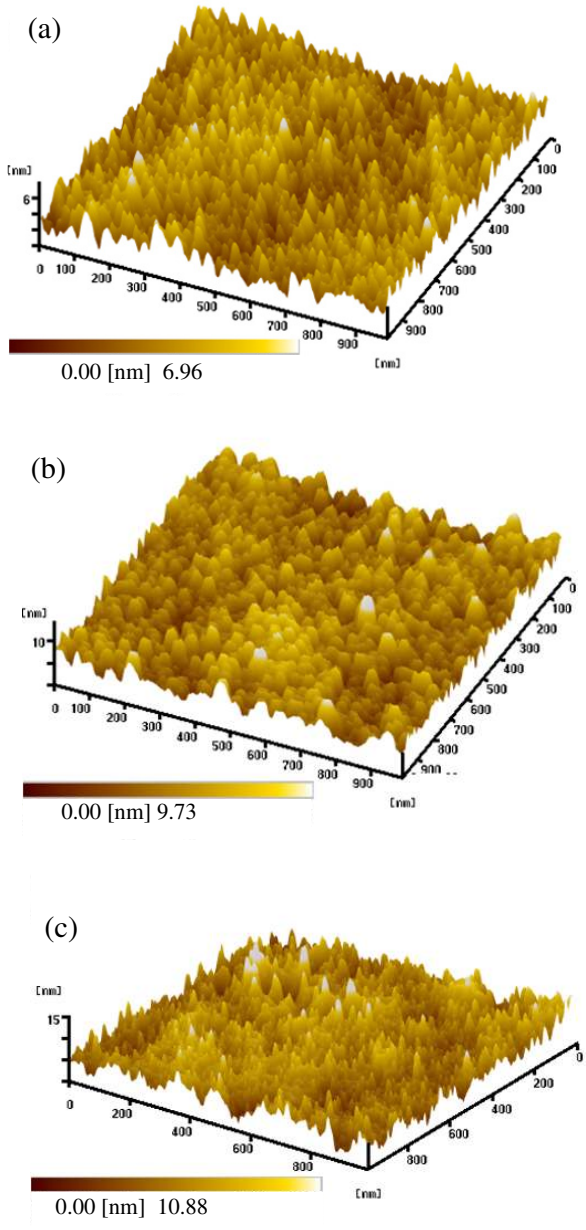

Figure 3. AFM three-dimensional images of PZT thin films, which were crystallized at (a) 400 °C, (b) 450 °C and (c) 600 °C.

saturated up to 550 °C, and then increased. The dielectric and ferroelectric properties were higher than that of the reported value of 2.45 GHz microwave-annealed PZT thin films [15].

4. Discussions

The crystal structures of films reveal that the 450–550 °C films have a pure perovskite phase with better crystallinity than the other annealed films, as shown in figures 1(a) and (b). The secondary phase (pyrochlore) appeared at 600 °C, which is attributed to PbO volatilization. The formation of the unwanted (secondary) pyrochlore phase at too high an annealing temperature was the result of the loss of lead

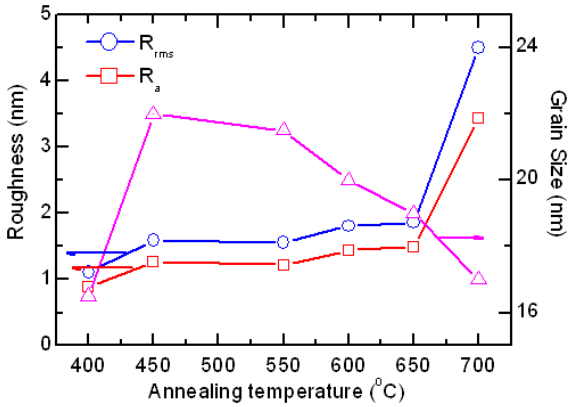

Figure 4. Surface roughness of PZT thin films as a function of the annealing temperature.

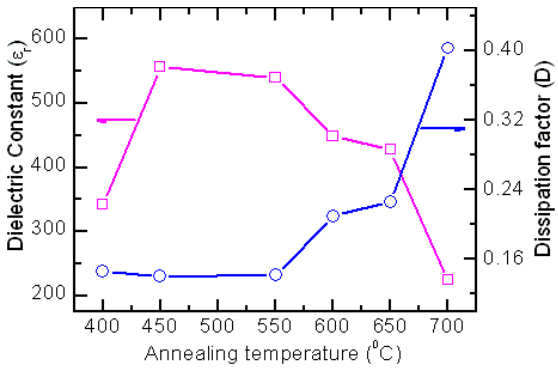

Figure 5. Dielectric properties of PZT thin films as a function of the annealing temperature.

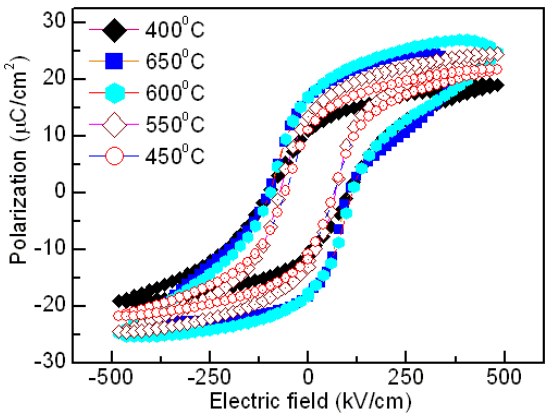

Figure 6. Polarization–electric field hysteresis loops of PZT thin films as a function of the annealing temperature.

oxide [21]. The low temperature annealed films had narrower FWHM than films annealed at higher temperatures due to PbO volatilization, which is in good agreement with an earlier report [25]. Chang *et al* [25] studied the effect of annealing temperature on the PZT thin films using the XRD technique and reported that too high an annealing temperature leads to the volatilization of PbO, which led to the poor quality of the PZT thin films. Such a (secondary) pyrochlore phase has

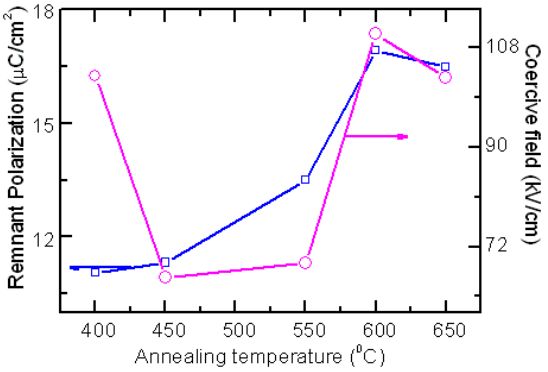

Figure 7. Remnant polarization and coercive field of PZT thin films as a function of the annealing temperature.

been reported by others for films held at 775 °C for 1 h [28], 880 °C for 1 h [29] by conventional annealing and 850 °C [30] by rapid thermal annealing. Generally, the conventionally annealed PZT thin film perovskite phase occurs at above 600 °C [1] and PbO is volatilized at above 775 °C [28, 29], but the microwave-annealed PZT thin film perovskite phase occurred at 450 °C and PbO was volatilized at above 550 °C (figure 1). Therefore, the microwave annealing is more effective than conventional annealing. The low temperature can be ascertained by the smaller grained microstructure (figure 2) in comparison with the conventional process [9]. The microwave is capable of rapidly heating the film with shorter processing time, which may lead to the suppression of the movement of grain boundaries [31]. Furthermore, the microwave driving force reduced the Pb atoms exceeding the energy barrier to transform the pyrochlore to the perovskite phase at low annealing temperature (450 °C). On the other hand, violently resonating the PZT lattice during a higher annealing temperature such as 600 °C might be the result of PbO volatilization to form the pyrochlore phase, as shown in figures 1–4. Therefore, the temperature of PbO loss in the microwave annealing process is far lower than the conventional annealing process. The PZT film crystallized at 600 °C shows large grains, and large grain sizes increased with annealing temperature (700 °C) which might be due to the (secondary) pyrochlore phase. Lee *et al* [26] reported that the pyrochlore phase was observed at 950 °C and large grains were observed in the SEM picture due to PbO evaporation. Zhu *et al* [21] reported that the (secondary) pyrochlore phase was formed at 700 °C, and its x-ray photoelectron spectrometry (XPS) indicated that the composition of the PZT films was rapidly changed with the evaporation of PbO, resulting in the formation of the pyrochlore phase again. The PZT thin film crystallized at 600 °C shows (AFM) non-uniform morphology. Brankovic *et al* [27] reported that the PZT thin film crystallized at 800 °C has a (secondary) pyrochlore phase and its AFM grain morphology was completely changed. Hamedi *et al* [32] reported that the surface roughness was changed with the deposition temperature of PZT thin films due to the lead content starting to vanish. The average grain size follows the same trend as the surface roughness of PZT thin films, as shown in figure 4. Based on the results presented in figures 3 and 4, it appears that the R_a and R_{rms}, size of the grains and their structures were strongly affected by the secondary phase. The grain size of the PZT thin films is within the range of ∼25 nm which is less than for the conventionally annealed PZT thin films [9]. The dielectric and ferroelectric properties of 450 and 550 °C microwave-annealed films have better properties than other annealed films (figures 5 and 6). The 450 and 550 °C PZT thin films show slim hysteresis loops and the 600 °C, 650 °C PZT thin films yield broad hysteresis loops possibly due to PbO volatilization [29]. Zheng *et al* [30] reported that the PZT thin film crystallized at 850 °C has a (secondary) pyrochlore phase and its hysteresis was changed. The PZT thin film crystallized at 700 °C does not show the hysteresis loop, which might be due to the PbO over-volatilization. Because of this, a crack was observed, which is attributed to the difference in thermal expansion coefficients of Pt (8.9×10^{-6} °C^{-1}) and PZT thin film (9.0×10^{-6} °C^{-1}). The E_c initially decreases with temperature between 400 and 450 °C, beyond which it saturated up to 550 °C and then increased, which is attributed to the trend of grain size variation. It has been widely reported in the literature that, with the decrease in grain size, E_c increases as each grain is mechanically clamped by its surroundings [33]. The dielectric and ferroelectric properties were higher than the reported values of 2.45 GHz microwave-annealed PZT thin films [15].

5. Conclusions

Complete PZT perovskite content at low temperature (450 °C) was obtained by 2.45 GHz microwave annealing. The annealing temperatures strongly affected the crystal structure, the microstructure and the surface morphology of the films. The secondary phase occurred in the PZT thin films when the annealing temperature was above 550 °C. Better dielectric and ferroelectric properties were obtained between 450 and 550 °C for the PZT thin films. The shapes of the hysteresis loops changed, reflecting the crystallinity. High diffusion rate of grain boundaries enhancing the perovskite phase at low temperature (450 °C) could be a contribution of the microwave annealing process.

Acknowledgments

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